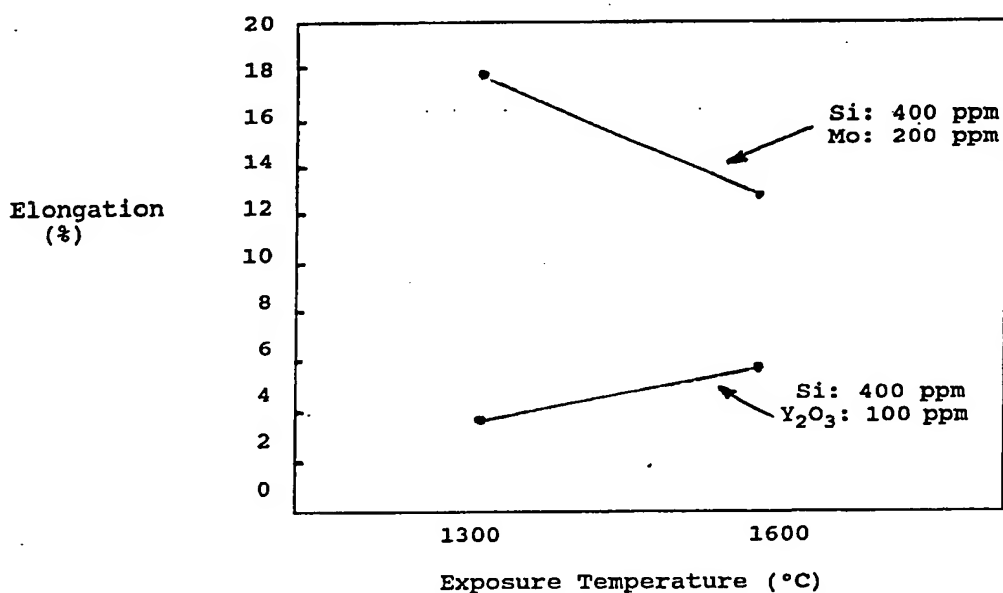


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(54) Title: TANTALUM OR NIOBIUM BASE ALLOYS**(57) Abstract**

A wrought metal alloy product having a tantalum or niobium base metal, 25 to 1000 ppm silicon, and 25 to 1000 ppm molybdenum. Fine uniform grain size contributes to improved tensile strength, processability, and high temperature stability.

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TANTALUM OR NIOBIUM BASE ALLOYS

Background of the Invention

The present invention pertains to the field of wrought metal base alloy products with improved chemical and physical characteristics, and more particularly to products of tantalum or niobium metal base alloys containing quantities of silicon and molybdenum

Tantalum alloy powders have been recognized as preferred materials in the field of furnace equipment: such as trays and heating elements, and radiation shielding where the thermal stability of the alloy is maintained and the life span of the product is enhanced by reduced embrittlement. Tantalum alloy have also been employed in the manufacture of wire and more particularly as electric component leads where product characteristics such as ductility, high dielectric constant and resistance to grain growth at elevated temperatures, and improved processability are required. In the production of capacitors, for example, the lead wires may either be pressed with the tantalum powder anode and subsequently sintered at high temperatures, or spot welded to sintered capacitor bodies. See U.S. Patent No. 3,986,869. In both electrical component and furnace equipment products, contamination by oxygen contributes to embrittlement. and piece failure. For example, in wire products, the area where a lead leaves an anode body is highly susceptible to embrittlement. due to migration of oxygen from the sintered body to the wire. Substantial economic benefit can be gained from a tantalum or niobium base alloy which does not lose strength or ductility after exposure to high temperatures. The tensile strength and ductility of wire

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are important characteristics. Once produced by a series of extrusion, rolling, and drawing steps, the annealed wire is transported to spools for shipment through a series directing pulleys and wheels. The ability of the wire to withstand the tensile forces prior to spooling and afterwards, prior to despooling and cutting by the consumer, is highly desirable.

The tensile strength and ductility are also desirable characteristics for furnace products. Furnace trays for example, encounter various handling and vibrational stresses with prolonged use. The enhanced strength and ductility results in prolonged product life.

For purposes of simplicity, reference hereafter will be made solely to tantalum even though it is understood that niobium is also contemplated.

The term "ductility" is a physical characteristic synonymous with reduced embrittlement. The term is typically understood to mean a percentage increase in length of the metal at the point prior to failure in a tensile test.

Oxygen embrittlement occurs in tantalum base alloy products by several mechanisms. Tantalum acts as a getter for oxygen in addition to other gaseous impurities present in sintering operations such as carbon monoxide, carbon dioxide, nitrogen, and water vapor. Attempts have been made to reduce tantalum oxide formation by doping tantalum with carbon or a carbonaceous material. Oxygen reacts with the carbon at the surface of the metal rather than diffusing into the tantalum thereby minimizing embrittlement. While enhanced ductility levels may be achieved with carbon addition, the dopant may adversely effect the processability and electrical characteristics of the metal. Carbon particles on the surface of the tantalum may result in increased electrical leakage due to the non-uniform adherence of tantalum oxide film.

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The term "dopant" is known to those skilled in the art as a trace material which is normally added to a base material. The term "processability" is also known in the art and is defined here after as the ratio of tensile strength to yield strength. Processability is measured by mechanical evaluation of tantalum alloy by a variety of methods including standardized ASTM testing referenced hereafter.

U.S. Patent Nos. 4,128,421 and 4,235,629 disclose the addition of silicon and/or carbon to tantalum to increase ductility. Silicon is volatilized in part during processing and therefore must be added in excess in the original master blend. Added costs are thereby incurred without a measured increase in product quality. While it is speculated that silicon functions as a getter similar to carbon, the addition of excess silicon may effect the electrical characteristics of the wire product by the same mechanism described above for carbon or carbonaceous materials.

Tantalum base alloys have also been prepared with high concentrations of molybdenum. U.S. Patent No. 3,183,085 discloses the production of wrought members from cast members composed of a tantalum alloy containing from 1 to 8% molybdenum (10,000 to 80,000 ppm).

The doping of tantalum powder with phosphorus is generally disclosed in U.S. Patent Nos. 3,825,802, and 4,009,007 as a means for improving the electrostatic capacity of capacitors and flow properties of the tantalum powders. Some significance is attributed to the amount of dopant added in the '007 patent (ranging from 5 to 400 ppm). Although the mechanism by which phosphorous functions as a dopant to tantalum metal is not completely known, one theory is that it reduces the sintering rate of tantalum by decreasing the surface diffusion of tantalum.

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Another mechanism for reducing the embrittlement of tantalum base alloy products involves the doping of tantalum powder with oxides of yttrium or thorium. Metal oxides act to reduce grain growth by pinning the grain boundaries. Metal oxides typically have lower Gibbs free energy and have elevated boiling temperatures in comparison with tantalum and therefore do not diminish product quality by the mechanism discussed above for silicon dopants.

U.S. Patent No. 3,268,328 discloses the doping of tantalum with small quantities of rare earth metals and oxides. Average grain sizes of 4 to 6 (ASTM) were optically determined from tantalum doped with yttrium oxide at temperatures between 1,815 and 2,204°C.

The term "grain size" may be defined as the number of grains or particles of tantalum as compared with a standard ASTM grain size chart at 100X magnification. The term "fine grain size" may be defined to mean an ASTM value of greater than 5 or less than about 55 microns. The term "uniform grain size" refers to a grain size which does not vary by more than one ASTM number according to the testing procedure discussed above.

Metal oxides, including oxides of rare earth metals, are not stable after being subjected to elevated temperature conditions such as are encountered in furnace environments. Although the mechanism is not completely understood, one theory accounting for dopant particle growth or "dispersant coarsening" is that the coarsening occurs due to the high diffusion rate of oxygen and metal atoms of oxides in refractory metals and is driven by the interfacial energy of the dispersoids. Enlarged dispersant particles have lower surface energy and therefore cannot function to restrain grain boundary migration. Grain growth in turn, results in loss of ductility.

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The combination of dopants in tantalum base alloys for wrought wire applications is disclosed in U.S. Patent No. 4,859,257. The patent discloses an alloy formed by adding 125 ppm silicon and 400 ppm thorium to tantalum powder. An ASTM grain size No. 10 and grain size No. 5 are obtained for a doped and an undoped control of pure tantalum powder. This translates into a doped tantalum base alloy grain size of 10 microns in comparison to a control of 55 microns. It is maintained that the mechanisms where silicon functions as an oxygen getter and where metal oxide functions as a grain boundary restraint, explain the basis for the reported fine grain size and ductility. The mechanisms, however, suffer from previously discussed problems of product quality due to silicon evaporation and grain growth after exposure to high temperatures due to dispersant particle growth. A tantalum based alloy which provides consistently high ductility and processability after exposure to high temperatures would be a considerable advance in the field of tantalum metallurgy.

Another object of the present invention is to provide tantalum alloy which maintains processability and ductility with low concentrations of dopants.

A further object of the present invention is to provide a doped tantalum alloy which maintains a high level of processability and ductility and wherein the dopants resist coarsening after exposure to high temperatures.

Yet a further object of the present invention is to provide a wrought wire product from tantalum base alloy which maintains processability and ductility, and which minimizes DC electrical leakage.

Accordingly, the present invention alleviates the above mentioned problems and achieves the cited objectives in a wrought metal alloy product where the alloy is formed from the addition of about 25 to about 1000 ppm silicon, about 25 to about 1000 ppm molybdenum, to a tantalum or niobium base metal. The doped tantalum alloy exhibits a fine

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uniform grain size of about 20 to about 55 microns. The inventor has discovered that the unexpected physical and chemical properties of the invention are largely due to the synergistic effect of silicon and molybdenum dopants.

The formation of molybdenum disilicide is unexpected due to the small quantities of silicon and molybdenum added. One skilled in the art would expect a mechanism where silicon competes as a getter with tantalum for available oxygen and trace gasses. Similarly, one skilled in the art would expect that wrought wire products made from such doped alloys would be of non-uniform ductility due to the low boiling temperature of silicon oxide.

The formation of molybdenum disilicide leads to an alloy which includes the characteristics of improved ductility, a high degree of processability, and which resists grain growth after exposure to elevated temperatures of less than about 1600°C.

A further advantage is that molybdenum disilicide has a higher boiling temperature than silicon and is more resistant to dispersant particle growth than metal oxides such as yttrium or thorium oxide.

A further advantage is that excess quantities of dopant formerly needed to replace evaporated silicon are not required. The grouping of excess dopant on the surface of the wrought alloy product and the associated problem of discontinuous tantalum oxide insulating, is also alleviated.

Brief Description of the Drawings

The disclosed objects, features, and advantages are further illustrated by the drawings, detailed description, and claims presented below.

Figure 1 illustrates two microphotographs of tantalum wire doped with silicon and molybdenum, and with silicon and yttrium oxide, after annealing for two hours at temperatures of 1300°C;

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Figure 2 illustrates two microphotographs as in Figure 1 annealed at 1600°C;

Figure 3 is a graph of the ductility of tantalum doped with silicon and yttrium oxide and tantalum doped with silicon and molybdenum verses the period of exposure to temperature;

Figure 4 shows electron diffraction patterns of tantalum doped with silicon and molybdenum as discussed in Example 7 illustrating the presence of molybdenum disilicides; and

Figure 5 is a dark field transmission electron micrograph illustrating the morphology of molybdenum disilicide precipitation.

Detailed Description of a Preferred Embodiment

Referring to Figures 1 and 2; two sets of photomicrographs were taken of .0094 inch diameter wire after annealing at temperatures of 1300°C and 1600°C in vacuum furnace; with the Figure 1 exposed to 1300°C and the Figure 2 exposed to 1600°C, each for two hours. As illustrated, tantalum wire doped with 100 ppm yttrium oxide and 400 ppm silicon exhibits incomplete recrystallization and non-uniform grain structure. As explained above, the non-uniform grain structure may be attributed to the coarsening of yttrium oxide particles. In comparison, the photomicrographs of Figures 1 and 2 made according to the procedure of Example 1 below, exhibit fully recrystallization and uniform grain structure.

Figure 3 illustrates in improved ductility in the present invention as produced by way of Example 1 of from 12.6 to 17.5 in comparison to 3.7 to 5.9 as found by way of the tantalum based wire doped with silicon and yttrium oxide of Example 3.

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Figure 4 illustrates a selected area electron diffraction pattern of tantalum sheet as presented in Example 7. The relative positions and intensities of the diffraction spots are indicative of molybdenum disilicide, as known to those skilled in the art.

Figure 5 illustrates the morphology of precipitates as determined by a dark-field transmission electron-micrograph of an area associated with the diffraction spot under the pointer in Figure 4.

The tantalum base wire of Figures 1-3 are made generally from a process where tantalum powder is blended with silicon and molybdenum powders by mechanical means such as a twin cone blender. The blended powder is cold isostatically pressed into bars at 60,000 PSI. The bars are then placed in a vacuum chamber and sintered by direct resistance sintering at between 2350 to 2400°C for about 4 hours.

The doped tantalum bar stock may be used to generate a variety of wrought products including furnace trays and leads for electronic components. For simplicity purposes the following description and examples pertain to wrought wire products.

Wrought wire is made from the sintered bars by rolling to a 20mm by 20mm cross-section followed by annealing. This is accomplished at 1300°C for two hours and is typically done in a standard vacuum furnace. The annealed bar is then rolled to a cross-section of 9mm by 9mm and reannealed at 1300°C for two more hours. Further processing is accomplished by drawing through various dies and annealing at 1300°C.

The tantalum powder may be made by several methods including the processes disclosed in U.S. Patent No. 4,684,399, assigned to the present assignee, Cabot Corporation. The process disclosed in Columns 4, 5 and Examples 2-9 are incorporated by reference herein.

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Example 1

Tantalum powder was blended with silicon and molybdenum powders (nominal particle size <200 mesh) to obtain a nominal composition of 400 parts per million of silicon and 200 parts per million of molybdenum by weight with the balance tantalum powder. Blending was accomplished in about 2 minutes in a twin cone blender. The total weight of the blend was about

50 pounds. Physical chemical properties of starting tantalum powder are given in Table 1 below. The blended powder was cold isostatically pressed into two bars at 60,000 PSI; each bar weighed about 22 pounds. The cross-section of the bar was about 41mm x 41mm. Bars were sintered by direct resistance sintering in a vacuum furnace. The temperature during sintering was 2350 - 2400°C. Bars were maintained through this temperature range for about 4 hours.

Sintered bars were rolled to a 20mm x 20mm cross-section and annealed at a temperature of 1300°C for a period of about 2 hours. The bars were then rolled to 9mm x 9mm and reannealed at 1300°C for an additional 2 hours. As stated above, bars are subsequently drawing through various dies and annealed at a temperature of about 1300°C. The final wire diameter generated for purposes of the examples of the present invention is 0.249mm.

TABLE 1: PROPERTIES OF STARTING TANTALUM POWDERChemical Analysis

<u>Element</u>	<u>Concentration (ppm)</u>
C	10 ppm
O ₂	540
H ₂	<5
N ₂	<10
Others	Not Detected

Sieve Analysis

<u>Size</u>	<u>Wt%</u>
+60 Mesh	0
60/100 Mesh	0.16%
100/200 Mesh	23.2%
200/325 Mesh	31.12%
-325 Mesh	45.32%

Analytical ASTM test procedures were utilized to determine the particle size (B-214), grain size (B-112), and tensile strength and elongation (E-8), of the doped tantalum base powder and products of the present invention.

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Example 2

This example describes the manufacturing of a commercially available formulation. The micro alloying with thorium oxide was accomplished via the decomposition of thorium nitrate into thorium oxide during sintering. Solution of thorium nitrate was mixed with tantalum powder to give about 100 ppm of thorium by weight. The total weight of the blend was about 50 pounds. The physical and chemical properties of starting tantalum powder are given in Table 1 above.

The blended powder was cold isostatically pressed into two bars at 60,000 PSI; each bar weighed about 22 pounds. The cross-section of the bar was about 41mm x 41mm. Bars were vacuum sintered by direct resistance sintering. The temperature of sintering was approximately 2350 to 2400°C. Bars were maintained at this temperature for about 4 hours.

Sintered bars were processed into wire by the procedure discussed in Example 1.

Example 3

Tantalum powder was blended with silicon and yttrium oxide powders (nominal particle size \leq 200 mesh) to obtain a nominal composition of 400 parts per million of silicon and 100 parts per million of yttrium oxide by weight in predominantly tantalum powder. Blending was accomplished in about 2 minutes in a twin cone blender. The total weight of the blend was about 50 pounds. The physical and chemical properties of starting tantalum powder are presented in Table 1.

The blended powder was processed into bars and then wire by the procedure of Example 2.

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Example 4

Wires from Examples 1 and 3 were evaluated after annealing for 2 hours in a vacuum furnace at 1300°C and 1600°C. Figures 1 to 3 and Table 2 set forth the microstructural, physical, and mechanical characteristics of the wire. The lack of recrystallization, abnormal grain growth and associated poor ductility in the silicon and yttrium oxide containing wire are apparent.

TABLE 2: EFFECT OF HIGH TEMPERATURE EXPOSURE
ON THE PROPERTIES OF WIRE (0.249mm DIAMETER)

Temp. of Exposure Composition	Wire of Example 1 400 Si/200 Mo	Wire of Example 3 400 Si/100 Y ₂ O ₃
<u>1300°C</u>		
Grain Size in Micrometer	5.	Not fully crystallized
Micro Hardness (DPH)	172	234
T.S. (KSI)	87	117
Ductility (%)	17.8	3.7
<u>1600°C</u>		
Grain size (Micrometer)	8.7	Not fully recrystallized. Some grains as large as 60 micrometers
Micro Hardness (DPH)	217	242
T.S. (KSI)	101.5	101
Ductility (%)		12.6 5.9

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Example 5

Table 3 gives the microstructure, mechanical, and chemical properties of 0.249mm diameter annealed wire produced in Examples 1, 2, and 3. The microstructure of the wire produced by Example 3 is considerably different from those of Examples 1 and 2. This accounts for the higher tensile strength and lower ductility; both of their factors can adversely affect the processability of the wire.

TABLE 3: PROPERTIES OF WIRE (0.249 mm DIAMETER)

<u>Property</u>	<u>Wire of Example 1</u>	<u>Wire of Example 2</u>	<u>Wire of Example 3</u>
Tensile Strength (KSI)	77	73.4	90
Elongation (%)	23.6	24.5	20
Grain Size	4.9	6	Not fully crystallized
c (ppm)	40	45	65
O ₂ (ppm)	135	145	120
N ₂	30	35	15
Si (ppm)	260	--	250
Mo (ppm)	100	--	--
Th (ppm)	--	80	--
Y (ppm)	--	--	40

Example 6

Composition of Examples 1 and 2 were evaluated, at various intermediate stages for the room temperature tensile strength and ductility. Table 4 illustrates the results of such testing. The similarities in the listed properties indicate that the processability of the composition of Example 1 will be similar to the wire generated by the procedure of Example 2.

TABLE 4ROOM TEMPERATURE TENSILE PROPERTIES

<u>Example 1</u>	<u>Example 2</u>	
(Dia.) 2.13mm		
T.S. (KSI)	63.1	63.2
Ductility	31	31.4
(Dia.) 0.84mm		
T.S.in (KSI)	66.5	66.4
Ductility	20.4	20.8

Example 7

Composition of Example 1 was rolled into 0.33mm thick sheet. The 9mm x 9xx "annealed bar was rolled to 2.3mm thick sheet and annealed at 1300°C for 2 hours in vacuum furnace and rolled to 0.76mm thick sheet and annealed at 1300°C for 2 hours in a vacuum furnace. It was further rolled to 0.33mm thick sheet and annealed at 1300°C for 2 hours in a vacuum.

Discs were cut to about 250 micrometers in thicknesses using a slow speed diamond saw. The discs were then ion milled to a thickness of 50-100 micrometers and then electropolished in a 90% H₂SO₄ + 10% HF solution until it developed microperforations. Transmission electron microscopy was performed in the vicinity of the perforations.

Figure 6 gives a bright field electron micrograph of the sample. A selected area diffraction pattern is given in Figure 7. The diffraction pattern was analyzed for relative intensities (I/I₀) and inter-planar spacings (d in

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A^o) for various spots using standard methods in crystallography. A comparison of d and I/I for spots in Figure 7 with those reported in Table 5 for MoSi_2 confirms the presence of MoSi_2 .

The morphology of the precipitate was determined by dark-field transmission micrograph and is shown in Figure 5. The precipitate size is about 150A° .

TABLE 6

COMPARISON OF INTER-PLANER SPACING AND RELATIVE INTENSITIES IN FIGURE 6 WITH THOSE REPORTED FOR MoSi_2

Inter-Planer Spacing in A ^o		Relative Intensities	
<u>Fig 6.</u>	<u>MoSi₂</u>	<u>Fig 6.</u>	<u>MoSi₂</u>
2.202	2.17	100	100
0.941	1.017	30	20
0.825	0.792	30	50
0.875	0.841	5	30
1.473	1.468	60	20
2.074	1.992	15	16
1.212	1.229	15	10
1.155	1.147	5	10
1.052	1.046	10	4

Those of ordinary skill in the art will recognize that many changes and modifications can be made in the above description without departing from the spirit of the invention. It is to be understood that the invention is not to be limited by their theories or details except as set forth in the claims that follow.

I Claim:

1. A wrought metal alloy product comprising a tantalum or niobium base metal, said base metal doped with a quantity of silicon ranging from about 25 ppm to about 1000 ppm and a quantity of molybdenum ranging from about 25 to about 1000 ppm.
2. The wrought metal alloy product of Claim 1 wherein said alloy maintaining fine uniform grain size after exposure to elevated temperatures of greater than 1200°C.
3. The wrought metal alloy product of Claim 1 wherein said fine grain size is from about 10 to about 55 microns.
4. The wrought metal alloy product of Claim 1 wherein said product has a ductility of about 20% after exposure to elevated temperatures of greater than 1200°C.
5. The wrought metal alloy product of Claim 1 wherein said product has molybdenum silicide intermetallic precipitates as detected by transmission electron microscopy and electron diffraction pattern.
6. In a wrought metal alloy product, the combination of tantalum or niobium metal with about 100 to about 1000 ppm silicon and about 100 to about 1000 ppm molybdenum, said metal alloy having a fine grain size of about 10 microns to about 55 microns.
7. The wrought metal alloy product of Claim 6 wherein said product has a ductility of about 20% after exposure to elevated temperatures of greater than 1200°C.
8. The wrought metal alloy product of Claim 6 wherein said product has molybdenum silicide intermetallic

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precipitates as detected by transmission electron microscopy and electron diffraction pattern.

9. The wrought metal alloy product of Claim 6 wherein said tantalum base metal has a level of impurities of no more than 10ppm carbon, 300 ppm O₂, 5 ppm H₂, and 10 ppm N₂.
10. In a wrought metal alloy product, the combination of tantalum or niobium metal with about 100 to about 400 ppm silicon and about 100 to about 400 ppm molybdenum, said metal alloy having a fine uniform grain size of about 10 microns to about 55 microns after exposure to elevated temperatures.
11. The wrought metal alloy product of Claim 10 wherein said product has a ductility of about 20% after exposure to elevated temperatures of greater than 1200°C.
12. The wrought metal alloy product of Claim 11 wherein said tantalum base metal has a level of impurities of no more than 10 ppm carbon, 300 ppm O₂, 5 ppm H₂, and 10 ppm N₂.
13. In a metal alloy wire, the combination of tantalum base metal with about 100 to about 400 ppm silicon and about 100 to about 400 ppm molybdenum, said tantalum base metal having a level of impurities of no more than 10 ppm carbon, 300 ppm O₂, 5 ppm H₂, and 10 ppm N₂, said metal alloy having a fine uniform grain size of about 9 microns to about 25 microns after exposure to 1600°C.
14. The metal alloy wire of Claim 13, where in the said wire has a ductility of about 12% after exposure to temperature of greater than 1200°C.

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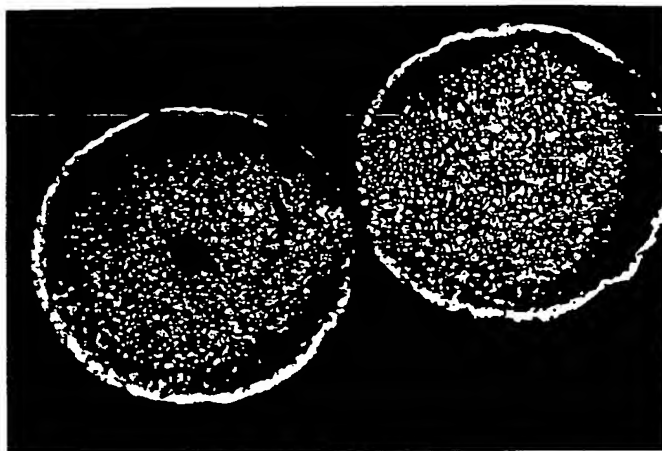


FIG. 1A



FIG. 2A

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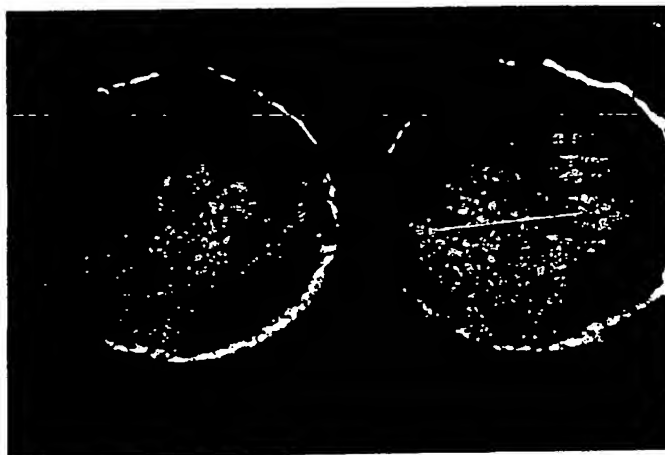


FIG. 1B



FIG. 2B

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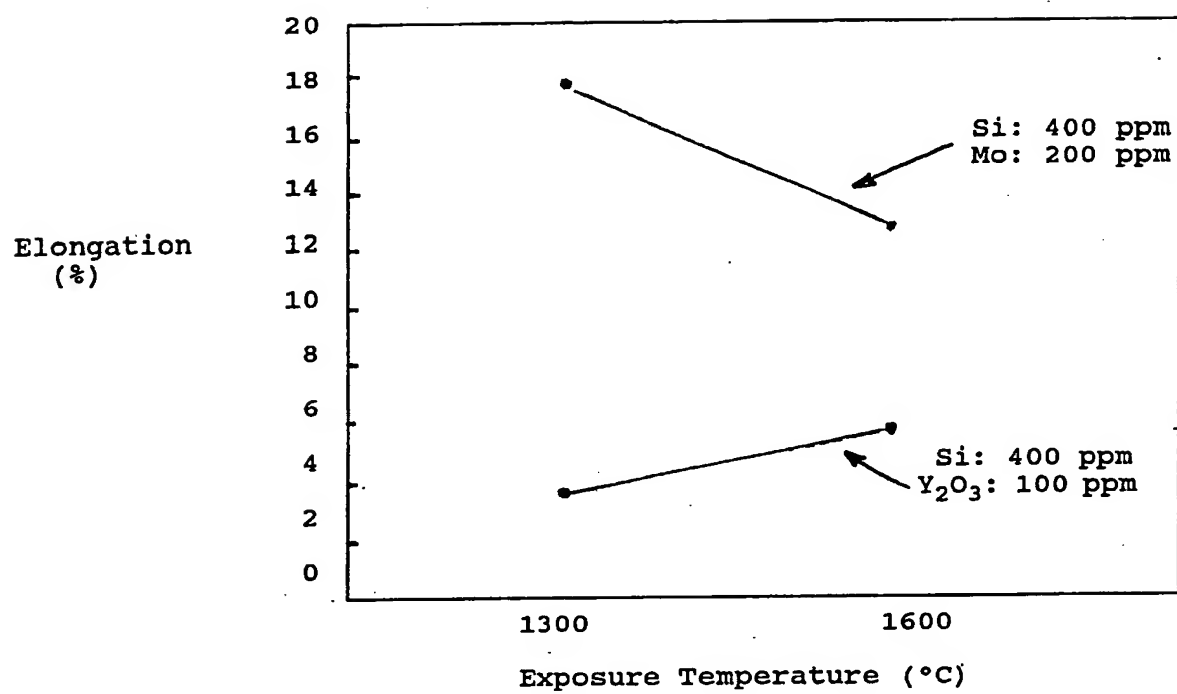


FIG. 3

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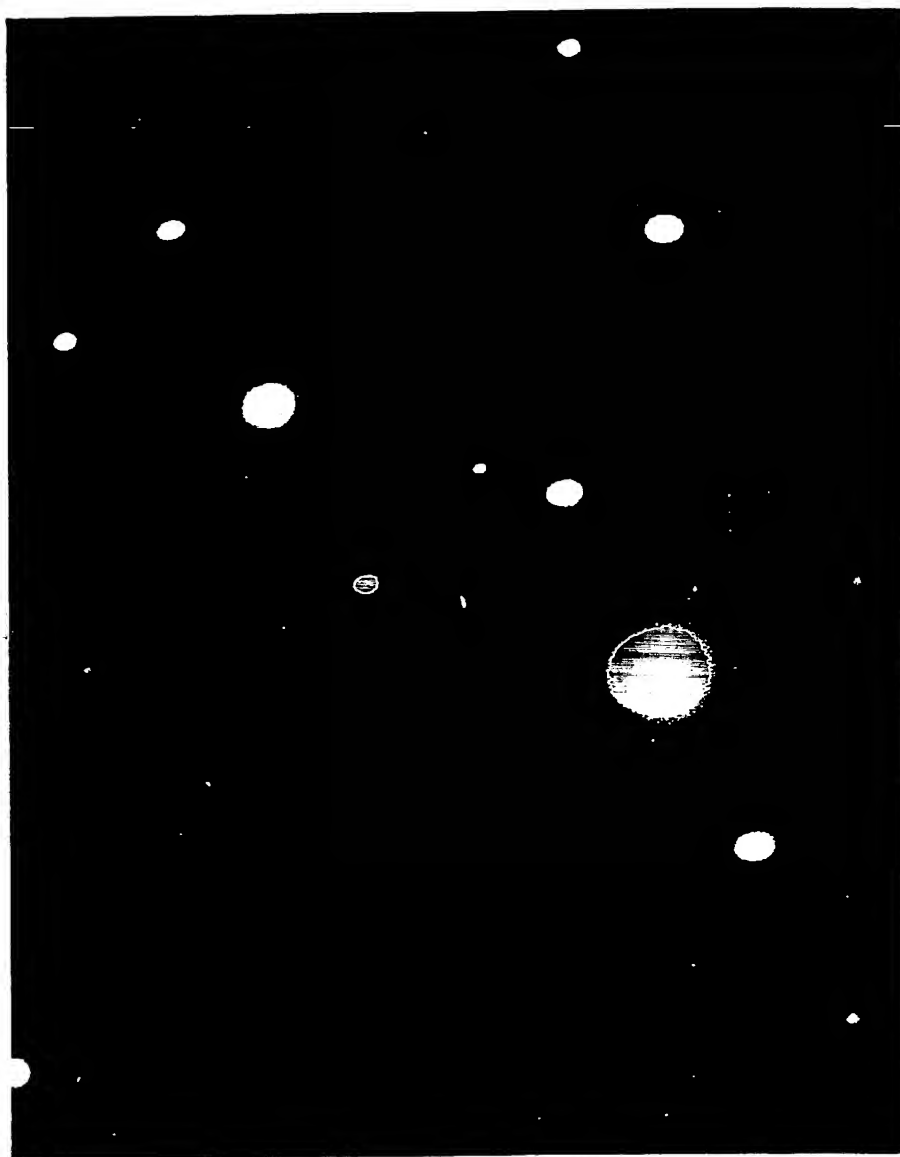


FIG. 4

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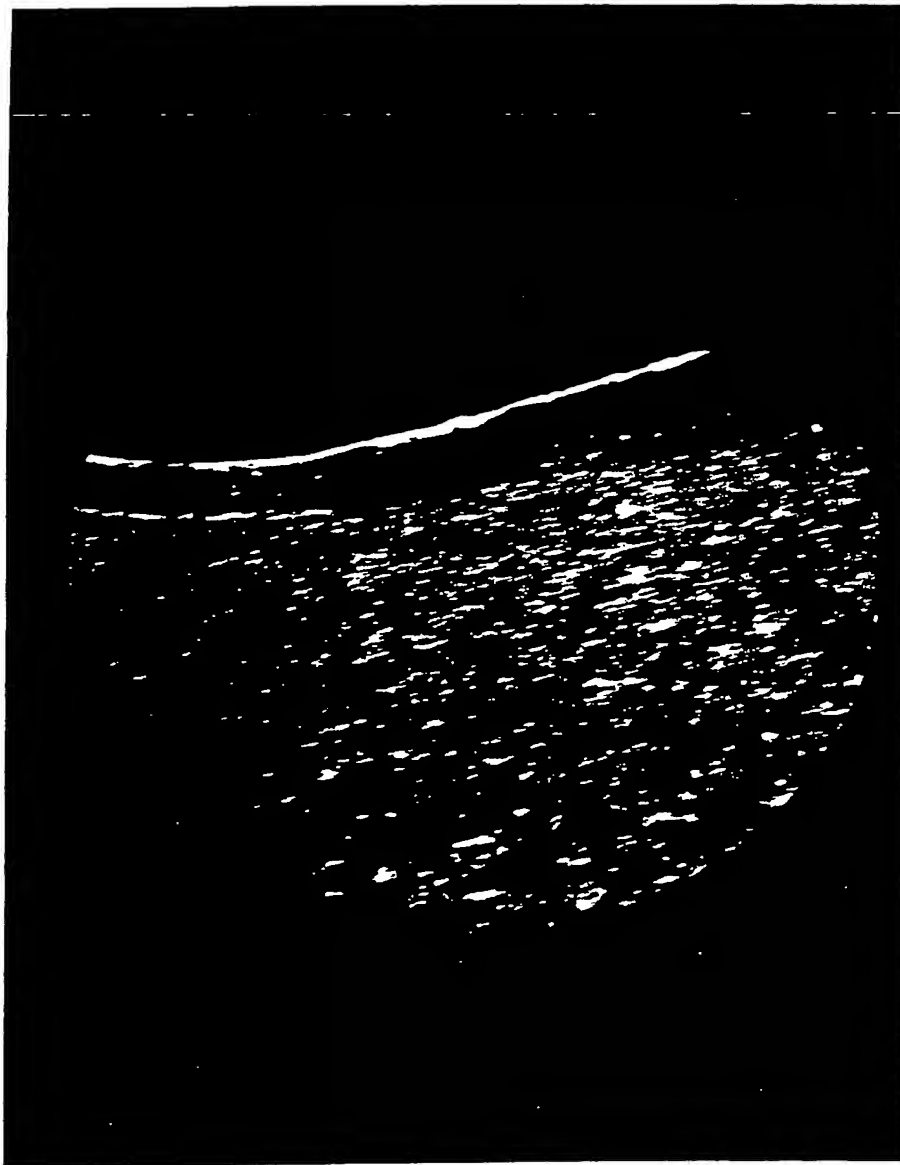


FIG. 5

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FIG. 6

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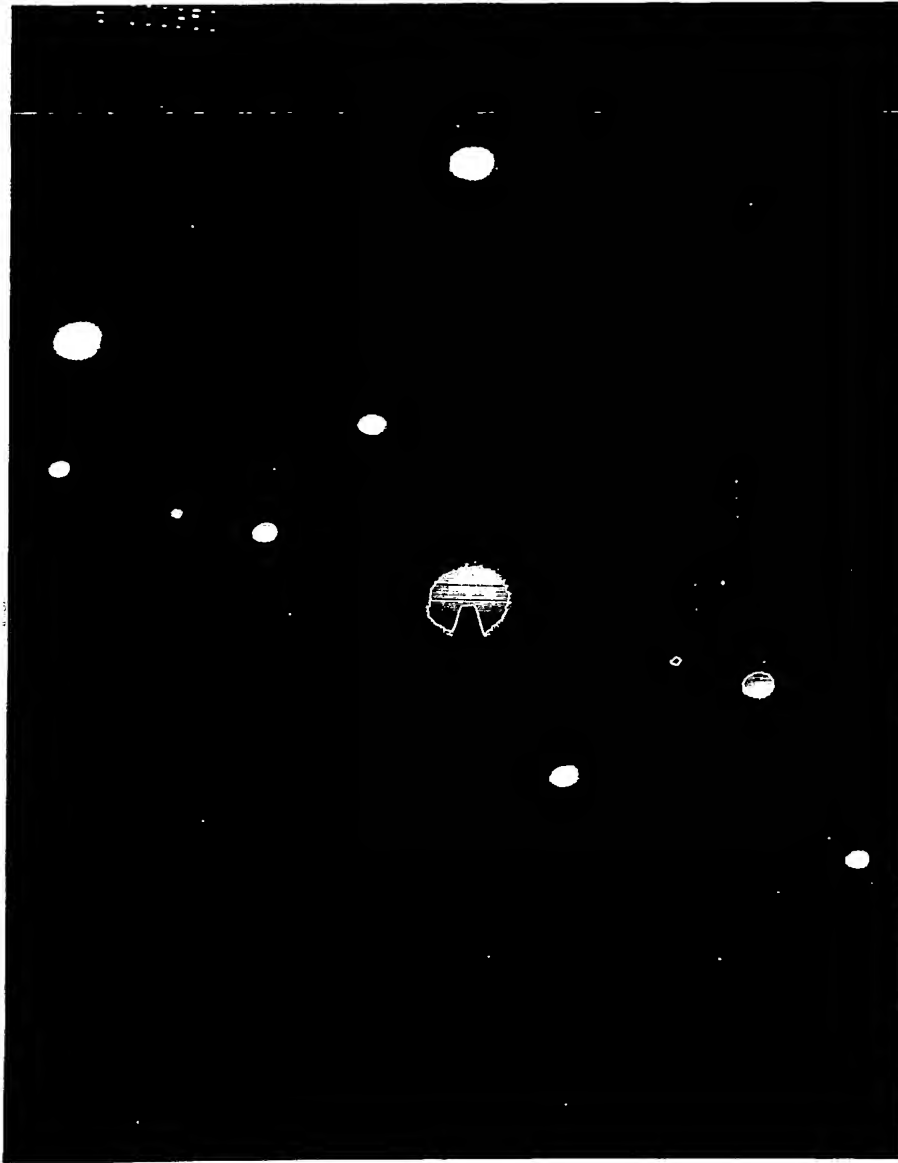


FIG. 7

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INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/03995

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC(5) C22C 27/00, B22F 1/00 US 148/422		
ii. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC(5) US	C22C 27/00 148/422, 420/425, 426, 427	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	US, A, 4,235,629, MARSH et al, 25 November 1980, See Example 3 on column 5.	1,6,10
A	US, A, 4,859,257, BATES et al, 22 April 1989, See entire document, Fig. 3.	1-14
X	US, A, 4,062,679, MARSH et al, 13 December 1977, abstract and example 3	1,6,10 and 14
Y,P	US, A, 4,957,541, TRIPP et al, 18 September 1990, see Figs. 1-2	1-14
Y	Journal of Metel, October 1989, MOSER et al, "The effects" of Silicon on the Properties of Tan- talam, USA, page 50, See table II	1-14
Y	Metallurgical Transactions, Vol. 13A June 1982, Gypen et al, "Athermal Solid Solution Hardening in Tantalum", p. 1015 see Figs. 3-4	1-14
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"Δ" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
27 August 1991	24 SEP 1991	
International Searching Authority	Signature of Authorized Officer	
ISA/US	U. Roy <i>M. Pandha Roy</i>	